

The Relationship Between Polymer Elastic Properties and the Ability to Impart Improved Wrinkle Recovery to Cotton Fabric

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Synopsis

The wrinkle recovery of polymer-coated cotton printcloth was generally found to correlate qualitatively with the elastic behavior of the polymer film. Of the several tensile parameters that can describe elasticity, immediate strain and work recoveries and stress decay were found to be the most sensitive indicators of the polymers' performance on the fabric. Delayed recovery, ultimate elongation, and permanent set were found to be important but were less sensitive parameters; while tensile strength and initial modulus appeared to be unrelated. A model is described whereby the polymer provides additional recovery forces when properly coupled to the fabric. High values of stress decay and permanent set diminish the effectiveness of these forces, while high values of immediate, work, and delayed recovery indicate that large portions of the distorting forces are available for recovery.

INTRODUCTION

In the past few years, research groups have demonstrated the ability of certain polymers to improve the wrinkle recovery behavior of cotton fabrics to which they had been applied.¹⁻⁶ In most cases the polymers were chosen primarily for their ability to improve the abrasion resistance and/or hand of a crosslinked fabric, rather than for their ability to improve wrinkle resistance, this latter property being an added dividend.

Until recently there appeared to be no clear distinction between various kinds of polymers, seemingly similar polymers being observed to yield widely differing results. Recent reports⁷⁻¹⁰ have however emphasized the importance of the elastic behavior of effective polymers. In an effort to further clarify these observations and to provide data from which a model could be developed, work was undertaken to establish whether or not a correlation exists between the tensile properties of a film cast from a given polymer and the wrinkle recovery imparted by that polymer.

EXPERIMENTAL

Based on past experience as well as on information available from the literature, at least two examples were chosen from each of four classes of polymers. Whenever possible, these were chosen in pairs such that one member of the pair imparted comparatively good wrinkle recovery to cotton fabric while the other did not. For the present purpose it was found satisfactory to use commercial samples, even though these were of an uncertain composition. The polyacrylates, referred to as Rhoplex K-3, HA-12, E-485, and E-477, were obtained in emulsion form from the Rohm & Haas Co. and were found to be based primarily on ethyl acrylate. The Kraton copolymers were supplied by the Shell Chemical Co. and are block copolymers that have styrene end blocks and a butadiene center block. The characteristics of this system are such that the components separate into two phases, or "domains." When cast from a solvent in which the butadiene segments are soluble, the styrene portion forms a discontinuous phase and acts both as a filler and as crosslinking sites between different copolymer molecules. Thus, these polymers require no curing to effect optimum elastic properties.¹¹

Two polyurethane sources were used. Those referred to as X-1033, X-1042, P102A, and E-503 are emulsions which were obtained from the Wyandotte Chemical Co. and consist primarily of polyethylene oxide and polypropylene oxide. The Estane polyurethanes, on the other hand, were obtained in solid resinous form from B. F. Goodrich and are based on a polyester structure.¹²

Several examples of polysiloxanes were obtained, two from the Dow-Corning Corp. and the others from General Electric. Those which are referred to as XET were emulsions of poly(dimethylsiloxane) which were formulated with two different silane crosslinking agents to yield a high modulus (#2) and a low modulus (#3) film.¹³ Those shown as SE-33 and SE-54 were obtained from General Electric as gum rubbers and applied from benzene solution. Both are primarily poly(dimethylsiloxane), but SE-33 has a small percentage of vinyl groups which replace some of the methyl groups, while SE-54 has a small amount of both vinyl and phenyl groups substituted for methyl groups. The polymer referred to as RTV-11 was also obtained from General Electric. It is a low molecular weight poly-(dimethylsiloxane)diol and was applied from cyclohexane solution in the presence of a crosslinking catalyst.

All of the polymers were applied to cotton printcloth samples by soaking the fabric in an emulsion or solution of the polymer with the concentration adjusted to obtain the desired weight add-on. Uniform distribution was facilitated by subsequently passing the sample through a two-roller padder. In cases where organic solvents were used, an attempt was made to put the treated fabrics on a comparable basis with those which had been treated with aqueous emulsions. In such instances the samples were soaked in water, after curing but prior to conditioning, until thoroughly wet.

After application of the polymer, the samples were dried and then cured in a forced-draft oven. The drying conditions (either under room conditions or in a vacuum oven at room temperature) and the curing conditions (time and temperature) varied somewhat from sample to sample and were adjusted according to recommendations found in the manufacturers' product bulletins. Air drying followed by curing at 150°C for 10 to 15 min was a common procedure. The styrene-butadiene copolymers required no curing. The K-3 and HA-12 polyacrylates and the several polyurethanes required no catalyst. The E-485 and E-477 polyacrylates used a 0.5% ammonium chloride catalyst, while the two General Electric polysiloxanes, SE-33 and SE-54, used a 1% benzoyl peroxide catalyst. Random checks of solubility in 0.5*M* cuene indicated that the cotton was not crosslinked.

In preparing films for testing tensile properties, solutions or emulsions were used which were two to ten times as concentrated as those used for fabric treatment. The solution was poured onto a plate glass panel and then swept out into a thin, even layer using a Gardner applicator. This layer was allowed to air dry in a dust-free room and was then cured in a forced-draft oven.

Film curing conditions were kept as nearly identical as possible to those to which the polymer-treated fabrics were subjected. Exact duplication was, however, prevented because the cast films were much thicker than the fabric coatings and therefore required a longer curing time. In addition, one side of the cast film was sometimes backed by a 1/4-in. glass plate during curing. This was necessitated whenever the strength of the air-dried film was insufficient to permit removal from the glass plate prior to curing. After curing, the films were conditioned overnight at 68°F and 65% relative humidity, as were the fabric samples, prior to testing.

Strips of the cast films to be tested were cut to 1-in. widths with a template and their average thickness were determined with a micrometer just prior to testing on an Instron testing machine, using a 10-cm gauge length. These were either subjected to a 5% elongation and allowed to relax immediately, or were held in the elongated configuration for 1 min. In either case, the relaxation rate was the same as the loading rate (5 cm/min), and all samples were allowed to relax further for 1 min before elongating and relaxing (immediately) a second time. The 1-min relaxation time was chosen because very little additional recovery could be observed at longer times.

Figure 1 describes the method of testing and evaluation and defines the terms as used in this work. The choice of nomenclature was made somewhat difficult by the deviations which were taken from standard testing procedures, together with variations in usage found in the general literature. The quantity which is termed "delayed recovery" is often found as "elastic" or "total" recovery, depending on the delay between the time when the stress is removed and the time at which the measurement is made. In the present case, an extra delay is imposed prior to stress removal. The term "immediate recovery" is similarly a compromise in terminology for a quantity that, when the sample is not held in an elongated configuration and

TABLE I
Comparison of Film Tensile Properties with Wrinkle Recovery Imparted by Treatment with Various Polymers^a

Polymer trade name ^b	Dealed recovery, %		Immediate recovery, %		Permanent set, %		Work recovery, %		Stress decay, %	Breaking elongation, %	Initial modulus, g/cm ²	WRA	
	WO	W	WO	W	WO	W	WO	W				Optimum add-on	at 5% add-on
Rhoplex E-477	89	62	40	18	16	38	34	3.5	75	152	1830	240/2	189
Rhoplex E-485	73	94	82	65	27	0	21	21	37	172	169	270/5	270
Rhoplex HA-12	99	27	50	8	0.8	2	19	24	76	429	738097	248/5	248
Rhoplex K-3	100	69	91	38	0	22	79	91	53	386	4915	270/2	270
Polyacrylates													
X-1042 (cured)	91		4	4		7		0.4	87	728	378	220/2	206
X-1042 (not cured)	94		12	12		5		2.7	74	665	329	220/2	206
X-1033	98		57	57		20		59	50	940	1396	250/5	250
Polyurethanes													
P102A	84	88	61	50	0	8	24	68	26	526	162092	216/11	202
E 503	100	88	88	50	0	8	69	68	26	1303	154229	250/4	250

Estane 5701-FI	92	79	6	16	696	1647	245/2	245
Estane 5703	95	71	0	24	804	298	245/2	245
Butadiene Copolymers								
Kraton 101 (cast from MIK) ^c	91	62	0	34	524		230/4	230
Kraton 101 (cast from et. acetate)	95	68	7	31	214		230/8	220
Polysiloxanes								
XET-4-0145 (No. 2)	120		115			10040	249/4	249
XET-4-0145 (No. 3)	99		76		103	673	248/2	240
SE-33	98	92	3.5	100	99	2550	260/21	240
SE 54	96	100	0.0	94	100	2163	280/16	250
RTV-11	91	91	9.0	85	5	146	260/24	233

^a WO = with, without holding the film elongated and requiring it to undergo extensive stress decay.

^b Trade names identified in text.

^c MIK = methyl isobutyl ketone.

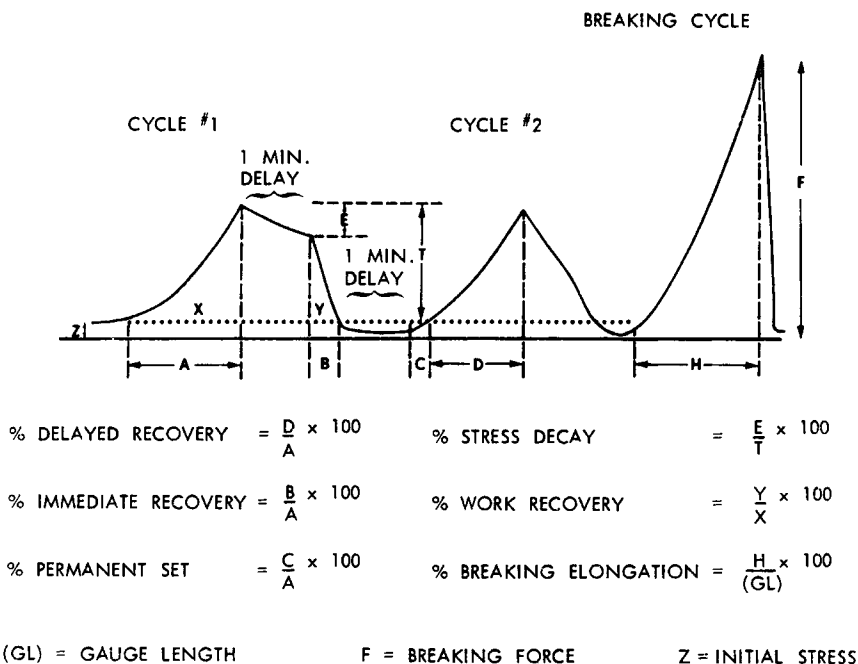


Fig. 1. Method of testing and evaluation of tensile properties of films.

required to undergo stress decay, is sometimes called "tensile" recovery. A more descriptive term might be "limited immediate-tensile-strain recovery," which reflects the fact that recovery was limited by the imposition of stress decay. The reader should carefully note the terminology as defined by Figure 1 before attempting to interpret the results.

Fabric samples were tested for wrinkle recovery angle (WRA) using the Monsanto technique (ASTM Standard 1295-60T). Control samples were treated in an identical manner, either water or the appropriate solvent replacing the emulsion of solution, respectively, during sample preparation.

RESULTS AND DISCUSSION

As mentioned, the various polymers were chosen in pairs such that one member imparted relatively good wrinkle recovery while the other did not. The recovery was measured over a wide range of add-on levels, and both the maximum WRA value obtained and the value at 5% add-on were used to compare with the various parameters extracted from the tensile data. The results are shown in Table I. The object was to obtain wrinkle recovery data for use in comparing polymer tensile properties with the ability of the polymer to improve the durable-press performance of the cotton fabric. Reasonable methods and techniques were used, but no attempt was made to optimize the conditions in order to obtain the highest possible recovery values.

Because the wrinkle recovery values reflect the recovery of each of the two components, the polymer and the fabric, as well as the coupling between these components, while the tensile data reflect only the behavior of the polymer, the comparisons should be confined to differences observed within a polymer pair. The trends in behavior can then be compared among polymer pairs, but no attempt should be made to compare the behavior of a given polymer in one pair with that of another polymer in a different pair. The polymers within a given pair are considered to be similar enough to eliminate variations in behavior which might result from differences in polymer-fabric coupling. Thus, any differences in wrinkle recovery behavior seen *within a polymer pair* can be compared with the tensile behavior of these polymers free of any differences superimposed by virtue of variations in polymer-fabric coupling. This is not true when comparisons are made among the several polymer pairs. Later experiments are planned from which it is hoped to obtain data which will allow such coupling to be considered to determine the total effect which the application of a polymer coating has in improving the wrinkle recovery of cotton fabric.

It can be seen from Table I that a number of qualitative correlations can be made between the WRA imparted to cotton printcloth and several of the tensile parameters. In nearly every polymer pair, the polymer imparting the higher WRA also has the higher immediate tensile recovery and work recovery. When the polymer film is held under stress, it is evident that this relationship is even more complete. This behavior is especially well illustrated by the polyacrylates HA-12 and K-3. Permanent set is generally greater, within a given pair, for the polymer with the lower WRA. This is accentuated also when the films are required to undergo stress decay, and it is particularly evident for polyacrylates E-477 and E-485. Of course, stress decay sets in as soon as elongation begins and continues until all stress has been removed from the film and strain has returned to zero. Therefore, samples which were not held for 1 min at a given elongation should nevertheless be considered to have undergone some limited stress decay.

High values of delayed recovery and breaking elongation are apparently necessary, but from Table I it would appear that, at best, wrinkle recovery is only a slowly varying function of these particular parameters. This can possibly be accounted for by the fact that delayed recovery (especially as measured here) includes a much longer time span for the polymer's recovery forces to operate than does immediate recovery. Thus the extent to which these forces are unavailable, which appears to be a major factor in determining the effectiveness of a given polymer in imparting fabric wrinkle recovery, is not as accurately accounted for by delayed recovery as it is by immediate recovery. These immediate recoveries (strain and energy, when not limited by stress decay) also correctly ranked the ability of crosslinked cotton yarns to recover.¹⁴

On the other hand, tensile strength (not shown in Table I) and initial modulus showed no correlation whatever with wrinkle recovery. For example, the high modulus version of poly(dimethylsiloxane) XET-0145

behaves insignificantly differently on the fabric from the low modulus version (#2 and #3, respectively). Likewise, the polyurethane pair P102A/E-503 have nearly the same initial modulus but impart very different wrinkle recovery angles to cotton printcloth.

The results indicate that the function of a deposited polymer, at least at the add-on levels reported here, is to couple in some way with the fabric's own recovery forces and thereby aid in overcoming the tendency to remain deformed. The load which an elastomeric polymer bears in helping to effect recovery will tend to make the polymer relax under stress and thereby diminish its ability to act in this way. Stress decay contributes to permanent set and is a time-dependent process. Its importance is readily understood when it is realized that in both the standard wrinkle recovery test and in normal apparel use, a polymer-treated fabric is held in a stressed (wrinkled) configuration for a certain period of time.

Other results from this laboratory indicate that several of the factors which affect the elastic behavior of a polymer film also have a marked effect on the resiliency which a particular polymer is able to impart to cotton fabric. The presence of weakening imperfections in a polymer film appears to detract from recovery, for example, and variations in curing conditions lead to large changes in imparted recovery. These observations support the above model but are as yet too incomplete for full discussion.

Another question that remains to be settled is the distribution of the polymer within the fabric and the means by which its recovery forces are coupled to those of the fabric. In several preliminary investigations, a statistically significant increase has been observed in the recovery properties of single cotton fibers which had been treated with several of the polymers discussed above. These observations have not yet been verified, but would imply that an elastic covering forms over the individual fibers and in this way couples with the fiber's own recovery forces, as has been proposed by Bullock and Welch.³ On the other hand, Rebenfeld and Weigmann,¹⁵ using scanning electron microscopy, have observed considerable interfiber bonding in the case of a polyurethane latex treatment. Both distributions have been observed on a rayon high-pile fabric, and it was concluded that fiber coating, rather than "spot welding," played the predominate role in determining fabric properties.⁸

CONCLUSIONS

The wrinkle resistance obtained by application of certain polymers to a fabric is a result of the elastic behavior of the polymer. The polymer forms an elastic film over the individual fibers or "welds" some fibers together, or perhaps both. Whatever the surface distribution, it is observed that the polymer contributes to the ability of the fiber assembly to recover from distortion. The extent of this contribution depends upon the coupling which occurs between the polymer recovery forces and those of the fabric and the bulk elastic properties of the polymer, of which immediate strain and work recoveries and stress decay are the most sensitive indicators.

Thus, the recovery of the polymer-coated fabric will depend in a general sense on the polymer's molecular weight, crosslink density, intermolecular attractive forces, crystallinity, and glass transition temperature—all factors which govern polymer elasticity. In addition, factors which influence the coupling between the fiber assembly and the polymer (e.g., the degree of physical bonding or adhesion which occurs between the polymer and the cotton surface, and the distribution of the polymer on the surface as a result of its wettability) will likewise affect the final behavior of the fabric-polymer composite.

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Use of a company or product name by the Department does not imply approval or recommendation of the product to the exclusion of others which also might be suitable.

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